

CLEAR, POLYMERIC GEL COMPOSITION AND
METHOD FOR PRODUCING THE SAME

RELATED APPLICATION

5 Pursuant to 37 C.F.R. § 1.78(a)(3) this application claims the benefit of U.S. provisional application serial number 60/315,402 filed August 28, 2002.

BACKGROUND OF THE INVENTION

10 1. **Field of the Invention**

This invention relates to the chemical arts. In particular, it relates to a polymeric gel composition and a method for producing the same.

15 2. **Discussion of the Related Art**

15 Clear, hydrophobic polymeric gel compositions have been described in U.S. Patent Nos. 4,497,663, 4,857,563, 5,780,527, and in WO 01/78792. It is a drawback of such hydrophobic gels, that the inclusion of water, even at extremely low levels, results in gels that are cloudy or opaque. It is a further drawback, that if water is included in these gels, the gels typically exhibit a “wetness” or syneresis, because of the incompatibility of the hydrophobic material and the water. It is a still further drawback that the hydrophobic gels are incompatible with many water soluble additives including pH color indicators, fluorescent dyes, water soluble dyes, water soluble fragrance components, and water soluble cross-linking agents.

20 Hydrophilic polymer compositions have been described in U.S. Patent Nos. 5,334,691 and 4,362,841. The gels have been shown to contain between 0.1-70 wt.% water. It is a drawback of these gels that when hydrophobic liquids, such as perfumes, insecticides, and insect repellants, are added, the gels are not clear, but are opaque, translucent, or heterogeneous.

25 Until now no system has been described that produces a gel composition, compatible with both hydrophobic liquids and water soluble materials, in a clear gel that is aesthetically pleasing and functionally appropriate.

SUMMARY OF THE INVENTION

Now in accordance with the invention there has been found a novel, clear, crosslinked, polymeric gel composition and a novel method for producing the gel 5 composition. The gel composition is the reaction product of a microemulsion containing (a) from 1-70 wt.%, preferably from 1-40 wt.%, and more preferably from 10-25 wt.% of an anhydride functionalized polymer, (b) from 0.1-40 wt.%, preferably from 0.1-20 wt.%, and most preferably from 0.5-5 wt.% of a cross-linking agent, (c) from 0.01-50 wt.%, preferably from 0.1-20 wt.%, and more preferably from 0.5-10 wt.% surfactant, (d) from 10 0.01-30 wt.%, preferably from 0.1-10 wt.%, and more preferably from 0.1-5 wt.% water, and (e) from 10.0-95.0 wt.% of a hydrophobic liquid, based on the total weight of the polymeric gel composition. In preferred embodiments, the combined proportion of (d) and (e) equals at least 30 wt.%, based on the total weight of the polymeric gel 15 composition.

15 Representative anhydride functionalized polymers include maleinized polybutadiene polymers, maleinized polyisoprene polymers, maleinized polybutadiene/styrene polymers or mixtures thereof. Representative cross-linking agents include polyamine cross-linking agents. Representative surfactants include anionic and nonionic surfactants. Representative hydrophobic liquids include perfumes, insecticides, 20 and insect repellants. In a preferred embodiment where the hydrophobic liquid is an insect repellant, the insect repellant is N,N-Diethyl-m-toluamide.

25 In some embodiments, the microemulsion additionally contains a water soluble additive. Useful water soluble additives include water soluble colorants, water soluble dyes, water soluble pH color indicators, water soluble pigments, water soluble fragrances, and water soluble flavor materials.

The gel composition is formed from a microemulsion that contains (a) from 1-70 wt.%, preferably from 1-40 wt.%, and more preferably from 10-25 wt.% of an anhydride functionalized polymer, (b) from 0.1-40 wt.%, preferably from 0.1-20 wt.%, and most 30 preferably from 0.5-5 wt.% of a cross-linking agent, (c) from 0.01-50 wt.%, preferably from 0.1-20 wt.%, and more preferably from 0.5-10 wt.% surfactant, (d) from 0.01-30 wt.%, preferably from 0.1-10 wt.%, and more preferably from 0.1-5 wt.% water, and (e) from 10.0-95.0 wt.% of a hydrophobic liquid, based on the total weight of the polymeric

gel composition. The microemulsion is then gelled to form the clear, crosslinked, polymeric gel composition.

In some embodiments, the microemulsion is gelled in a mold and the resulting gel composition is then removed from the mold. And in some embodiments, the 5 microemulsion is formed by combining a first premix containing the cross-linking agent and one or more of at least a portion of the hydrophobic liquid, the surfactant, and the water with a second premix containing the anhydride functionalized polymer and one or more of at least a portion of the hydrophobic liquid, the surfactant, and the water. In some preferred embodiments, the first premix contains the cross-linking agent, the 10 surfactant, the water, and a first portion of the hydrophobic liquid. And in some preferred embodiments, the second premix contains the anhydride functionalized composition, and a second portion of the hydrophobic liquid.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

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The present invention provides a clear, crosslinked, polymeric gel made from a microemulsion that contains (a) from 1-70 wt.%, preferably from 1-40 wt.%, and more preferably from 10-25 wt.% of an anhydride functionalized polymer, (b) from 0.1-40 wt.%, preferably from 0.1-20 wt.%, and most preferably from 0.5-5 wt.% of a cross-linking agent, (c) from 0.01-50 wt.%, preferably from 0.1-20 wt.%, and more preferably from 0.5-10 wt.% surfactant, (d) from 0.01-30 wt.%, preferably from 0.1-10 wt.%, and more preferably from 0.1-5 wt.% water, and (e) from 10.0-95.0 wt.% of a hydrophobic liquid, based on the total weight of the polymeric gel composition. In preferred embodiments, the combined proportion of (d) and (e) equals at least 30 wt.%, based on 20 the total weight of the polymeric gel composition.

The microemulsion contains from 1-70 wt.%, preferably from 1-40 wt.%, and more preferably from 10-25 wt.% of an anhydride functionalized polymer. Useful anhydride functionalized polymers are polymers made by reacting maleic anhydride with a suitable polymer, such as butadiene, isoprene, chloroisoprene, butadiene-styrene, other 30 polyunsaturated hydrocarbons, including mixtures thereof, resulting in a covalent attachment of maleic anhydride to the polymer.

Examples of suitable anhydride functionalized polymers include maleinized polybutadiene (such as Ricon 131MA10, available from Sartomer Co., Exton, Pennsylvania, and Lithene N4-9000-MA10, available from Synthomer Ltd., Essex, U.K.), maleinized polyisoprene (such as LIR-403, available from Kurary Co., Ltd., 5 Tokyo, Japan), maleinized polybutadiene-styrene (such as Ricon 184), maleinized polychloroisoprene, maleinized polybutadiene-isoprene, and maleinized vegetable oil. Maleinized polybutadiene and maleinized polyisoprene are preferred. Maleinized polybutadiene is most preferred.

The microemulsion also contains from 0.1-40 wt.%, preferably from 0.1-20 wt.%, 10 and most preferably from 0.5-5 wt.% of a cross-linking agent for the anhydride functionalized polymer. It is an advantage of the invention that the cross-linking agent can be a water soluble cross-linking agent. Representative water soluble cross-linking agents include polyoxyethylene diamine, such as Jeffamine D 2003.

Suitable cross-linking agents are materials that react with an anhydride 15 functionalized polymer to form a cross-linked polymer. Typically, the anhydride functionalized polymer and the cross-linking agent are included in a molar ratio of between about 3:1 and 0.5:1, preferably of about 1:1, based on the molar ratio of the functional groups which are present.

Representative cross-linking agents include, but are not limited to, compounds 20 that contain an amine, alcohol, or thio functional group. Suitable cross-linking agents can also contain a combination of one or more thio, amine and alcohol functional groups. Also useful are the solid, heat-activated cross-linking agents disclosed in U.S. Patent No. 5,844,047 (which patent is herein incorporated by reference).

Preferred cross-linking agents include polythios, polyols, and polyamines, with 25 polyamines being the most preferred cross-linking agent. Suitable polyamine cross-linking agents include (1) diamines, including polyoxypropylenediamine (such as Jeffamine D-400, available from Huntsman Corp., Salt Lake City, Utah) and triethyleneglycoldiamine (such as Jeffamine XTJ-504) and (2) triamines, including polyoxypropylenetriamine (such as Jeffamine T-403 and XTJ-509). Also useful are 30 hindered polyamines, such as the hindered polyamines described in U.S. Patent No. 5,633,341 (which patent is herein incorporated by reference) and polyamines contained

within molecular sieves, such as the polyamines described in U.S. Patent No. 5,792,816 (which patent is herein incorporated by reference).

The microemulsion contains from 0.01-50 wt.%, preferably from 0.1-20 wt.%, and more preferably from 0.5-10 wt.% surfactant. Suitable surfactants include nonionic 5 surfactants, amphoteric surfactants, zwitterionic surfactants, cationic surfactants, anionic surfactants and combinations thereof. Preferred surfactants are nonionic and anionic surfactants. Examples of nonionic surfactants are ethoxylated nonylphenol containing 4 moles of ethylene oxide (such as Surfonic N40, available from Huntsman Corp., Salt Lake City, Utah) and ethoxylated alcohols containing 3 moles of ethylene oxide (such as 10 Surfonic L24-3 and Tergitol 15-S-3, available from Dow Chemical Co., Midland, Michigan). Examples of anionic surfactants are ethoxylated alkyl sulfates (such as Steol CS460, available from Stephan Company, Northfield, Illinois).

The microemulsion contains from 0.01-30 wt.%, preferably from 0.1-10 wt.%, and more preferably from 0.1-5 wt.% water and 10.0-95.0 wt.% hydrophobic liquid. In a 15 preferred embodiment, the combined proportion of water and hydrophobic liquid equals at least 30 wt.%, based on the total weight of the polymeric gel composition.

Suitable hydrophobic liquids that can be used in accordance with the invention include, but are not limited to, hydrocarbons, including oils, such as aliphatic hydrocarbon oils and naphthenic hydrocarbon oils, such as paraffin oils, mineral oils, 20 vegetable oils, and kerosene, fatty esters, fatty acids, triglycerides, diglycerides, monoglycerides, alcohols, including polypropylene glycol and propoxylated or ethoxylated alcohols, ethers, amides, polyamides, cyclic hydrocarbons, propoxylated or ethoxylated acids, propoxylated or ethoxylated glycerides, silicon hydrocarbons, saturated or unsaturated synthetic oils, perfumes, hydrocarbon-containing fragrance raw 25 materials, including those containing alcoholic, cyclic, aldehydic, ether, unsaturation, sulfur, and keto functionalities, and essential oils, insecticides, and insect repellants. Useful insect repellants include any volatile insect repellant, such as pyrethroid insecticides, Citronella, citronellol, nerol, geraniol, and N,N-Diethyl-m-toluamide (DEET). A preferred insect repellant is DEET.

30 One advantage of this invention is the ability of the microemulsion to incorporate water soluble additives and the compatibility of the water soluble additives in the resulting clear polymeric gel. Examples of water soluble additives that can be included

in the microemulsion are pH color indicators, fluorescent dyes, water soluble dyes, and water soluble flavor and fragrance components. Specific examples include thymolphthalein and thymol blue pH color indicators.

Additionally, the present invention provides a method to produce the gel that 5 comprises vigorously mixing (a) from 1-70 wt.%, preferably from 1-40 wt.%, and more preferably from 10-25 wt.% of an anhydride functionalized polymer, (b) from 0.1-40 wt.%, preferably from 0.1-20 wt.%, and most preferably from 0.5-5 wt.% of a cross-linking agent, (c) from 0.01-50 wt.%, preferably from 0.1-20 wt.%, and more preferably from 0.5-10 wt.% surfactant, (d) from 0.01-30 wt.%, preferably from 0.1-10 wt.%, and 10 more preferably from 0.1-5 wt.% water, and (e) from 10.0-95.0 wt.% of a hydrophobic liquid, based on the total weight of the polymeric gel composition to form a microemulsion. In preferred embodiments, the combined proportion of (d) and (e) equals at least 30 wt.%, based on the total weight of the polymeric gel composition.

Vigorous mixing of the surfactant, water, and the hydrophobic liquid promotes 15 the formation of the microemulsion. Without wishing to be bound by a theory of the invention, it is believed that the microemulsion is characterized by the formation of water-in-oil micelles, that effectively minimize the diffraction of light in the visible wave-range.

The resulting microemulsion then reacts at ambient temperature and pressure to 20 gel and form a clear, cross-linked polymer gel. In some embodiments, the microemulsion is placed in a mold where gelling occurs. The resulting structurally stable gel is then removed from the mold.

In some embodiments, the microemulsion is formed by first making two 25 premixes, one containing the anhydride functionalized polymer and the other containing the cross-linking agent and then blending the premixes. For example, in one embodiment, the microemulsion is formed by combining a first premix containing the cross-linking agent and one or more of at least a portion of the hydrophobic liquid, the surfactant and the water with a second premix containing the cross-linking agent and one or more of at least a portion of the hydrophobic liquid, the surfactant and the water. In 30 some embodiments the first premix contains the cross-linking agent, the surfactant, the water and all the hydrophobic liquid. In alternative embodiments, the second premix contains the anhydride functionalized composition and all the hydrophobic liquid.

EXAMPLES

The following examples are intended to further illustrate the invention and not to limit it.

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Example 1

An aqueous gel was made using the following procedure. Premix A was made by combining 5.0g of fragrance oil and 1.9g of Lithene N4-9000-MA10 and mixed until homogeneous. Premix B was made by combining 2.4g fragrance oil, 0.1g water, 0.2g 10 Surfonic N-40 and 0.3g Jeffamine XTJ-403 and mixed until homogeneous. Premix A and Premix B were then combined and mixed vigorously for 15-30 seconds. This microemulsion was poured into a 2 inch diameter clear petri dish and the clarity was rated after the gel composition formed. The resulting gel was clear as seen in Table 1.

15 Example 2

An aqueous gel was made using the procedure described in Example 1, except that Premix B contained 2.5g fragrance oil and Jeffamine XTJ-509. The resulting gel was clear as seen in Table 1.

20 Example 3

An aqueous gel was made using the procedure described in Example 1 except that Premix B contained 2.6g fragrance oil and 0.2g Surfonic L-24-3 and 0.2 g Jeffamine D-400. The resulting gel was clear as seen in Table 1.

25 Example 4

An aqueous gel was made using the procedure described in Example 1 except that Premix B contained 2.6g fragrance oil and 0.2g Surfonic 15-S-3 and 0.2g Jeffamine D-400. The resulting gel was clear as seen in Table 1.

30 Example 5 (Comparative Example)

Aqueous gels were formed using the procedure described in Example 1 except as follows. Premix A contained 5.0g fragrance oil and 1.9g Lithene. Premix B contained

2.4g fragrance oil, 0.1g water, 0.3g Jeffamine T-403 and one of the following surfactants, (a) 0.2g Surfonic N85, (b) 0.2g Surfonic N120, or (c) a mix of 0.1g Surfonic N40 and 0.1g Surfonic N85. None of these gels were clear as seen in Table 1.

5 Example 6 (Comparative Example)

An aqueous gel composition was formed using the procedure described in Example 1, except that premix B did not contain a surfactant. The resulting gel composition was not clear as seen in Table 1.

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Table 1

	Experiment Number	Fragrance Oil	Lithene N4-9000-MA10	Water	Surfonic N40	Surfonic N85	Surfonic N120	Surfonic L-24-3	Tergitol 15-S-3	Jeffamine T-403	Jeffamine XTJ-509	Jeffamine D-400	Result (1)
15	1	7.4	1.9	0.1	0.2	-	-	-	-	0.3	-	-	Clear
	2	7.5	1.9	0.1	0.2	-	-	-	-	-	0.3	-	Clear
	3	7.6	1.9	0.1	-	-	-	0.2	-	-	-	0.2	Clear
	4	7.6	1.9	0.1	-	-	-	-	0.2	-	-	0.2	Clear
	5	7.4	1.9	0.1	-	0.2	-	-	-	0.3	-	-	Hazy
	6	7.4	1.9	0.1	-	-	-	-	-	0.3	-	-	Cloudy

(1) The clarity of each gel composition was judged on a scale ranging from clear, hazy, cloudy, and opaque.

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Example 7

An aqueous gel was made using the following procedure. Premix A was made by combining 10.0g of fragrance oil and 3.8g of Lithene N4-9000-MA10 and mixed until homogeneous. Premix B was made by combining 5.0g fragrance oil, 0.4g water, 0.5 g. 30 ethoxylated laural sodium sulfate, 0.1g ethanol, 0.33g Jeffamine D-400, and 0.1g Jeffamine XTJ-509. Premix A and Premix B were then combined and mixed vigorously for 15-30 seconds. This microemulsion was poured into a 2 inch diameter clear petri dish and the clarity was rated after the gel composition formed. The resulting gel was clear as seen in Table 2.

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Example 8

An aqueous gel was made using the procedure described in Example 7, except that Premix B contained 5.5 6g fragrance oil, 0.15g water, 0.3g ethoxylated laural sodium sulfate, and 0.05g ethanol. The resulting gel was clear as seen in Table 2.

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Example 9

An aqueous gel was made using the procedure described in Example 7, except that Premix B contained 0.3g water, 0.6g ethoxylated laural sodium sulfate, and 0.1 g ethanol. The resulting gel was clear as seen in Table 2.

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Example 10

An aqueous gel was made using the procedure described in Example 7, except that Premix B contained 4.6g fragrance oil, 0.3g water, 0.6 g. ethoxylated laural sodium sulfate, and 0.4 g Jeffamine T-403. The resulting gel was clear as seen in Table 2.

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Table 2

	Experiment Number	Fragrance Oil	Lithene N4-9000 MA10	TEA Water	Laural Sulfate	Alkyl Sulfonate Na salt	Ethoxylated Laural Na Sulfate	Ethanol	Jeffamine D-400	Jeffamine XTJ-509	Jeffamine T-403	Result (1)	
15	7	15.0	3.8	0.4	-	-	-	0.5	0.1	0.33	0.1	-	Clear
20	8	15.5	3.8	0.15	-	-	-	0.3	0.05	0.33	0.1	-	Clear
	9	15	3.8	0.3	-	-	-	0.6	0.1	0.33	0.1	-	Clear
	10	14.6	3.8	0.3	-	-	-	0.6	0.1	-	-	0.4	Clear

(1) The clarity of each gel composition was judged on a scale ranging from clear, hazy, cloudy, and opaque.

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Example 11

An aqueous gel was made using the following procedure. Premix A was made by combining 10.0g of fragrance oil and 3.8g of Lithene N4-9000-MA10 and mixed until homogeneous. Premix B was made by combining 4.8g fragrance oil, 0.3g water, 0.3g ethoxylated laural sodium sulfate, 0.1g ethanol, 0.4g Jeffamine D-400, and ca. 0.001g LX1926 Pylachrome Purple. Premix A and Premix B were then combined and mixed vigorously for 15-30 seconds. This microemulsion was poured into a 2 inch diameter clear petri dish and the clarity was rated after the gel composition formed. The resulting gel composition was clear and the purple color was uniformly distributed throughout the gel.

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Example 12

An aqueous gel was made using the following procedure. Premix A was made by combining 5.0g DEET and 1.9g of Lithene N4-9000-MA10 and mixed until homogeneous. Premix B was made by combining 2.2g fragrance oil, 0.15g water, 0.05g

ethanol, 0.4g Jeffamine T-3000. Premix A and Premix B were then combined and mixed vigorously for 15-30 seconds. This microemulsion was poured into a 2 inch diameter clear petri dish and the clarity was rated after the gel composition formed. The resulting gel composition was clear.

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Example 13

An aqueous gel was made using the procedure described in Example 12 except that Premix B contained 2.2 g of fragrance oil instead of DEET. The resulting gel was clear.

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Example 14 (Comparative Example)

An aqueous gel composition was formed as described in US Patent Number 4,362,841. Microemulsion A was formed by combining 10g fragrance oil, 10g maleinized polyisoprene (LIR-403), 1.0g Epicote 828, 0.5g Ancamine K-54 and 1.5g 15 Surfonic L-24-3. Into this microemulsion 0.1, 0.4 or 5.0g of water was slowly added while mixing. None of the resulting gels were clear.

Example 15 (Comparative Example)

An aqueous gel composition was formed as described in US Patent Number 20 5,334,691. The following materials were combined as described in the patent: 74.8g Carbowax 8000, 2.1g Diethylene Glycol, 22.1g Desmodur W, 1.0g water, 0.2g catalyst and 13.6g urea. The resulting gel composition was not clear.

The inventive gel compositions are compatible with both hydrophobic liquids and 25 water soluble materials and are aesthetically pleasing and functionally appropriate. It should be understood that the examples and embodiments described herein are for illustrative purposes only and that various modifications or changes in light thereof will be suggested to persons skilled the art and are to be included within the spirit and purview of this application and the scope of the appended claims.